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FAT POLYMORPHISM AND CRYSTAL SEEDING EFFECTS ON FAT BLOOM STABILITY OF DARK CHOCOLATE

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Abstract

The effects of seeding with fine crystal powders on the physical properties or dark phodolate are reviewed in terms of the polymorphism and crystallization behavior of cocoa butter (CB) and of its major fat constituents. The polymorphic structure of four symmetric mixed acids saturated-olaic-saturated (Sat-O-Satt triacylgiycerols (TAGs) (POP 1.3-dipalmitovl-2pieovi-givceroi);SOS(1,3-distearbyl-2-bieovi-giycerol); AOA - 1,3-diarachidoyi-2-oleoyi-glyceroll; and BOB 1.8-dibenencyl-2-diecyl-glycerol)], and of tristearcylgiveerol (SSS) are priefly explained. An attempt is made at replacing the currently used tempering method in the phocolate solidification process, by a simple cooling technique using fat seed crystals. CB (form VIII, SOS (β_1) , BOB (pseudo- β_1), BOB (β_2) , and SSS (β) are examined as seed materials. The addition of all powders accelerated the crystallization of dark chocoate. Fat ploom stability is also improved by the seed prystals, except with SSS. The effect is highly dependent on the physical properties of the seed material employed. The most influencing factors are the simifarities in the polymorphic behavior between the seed material and cocoa butter, especially, chain length structure. Thermal stability of the seed crystal is also very important. In view of all physical properties examined, the present review concludes that the eta_2 form of BOB performs pest as a seed material. In particular, it gives rise to an accelerated crystallization of form V of CB and moderates change in viscosity and antibloom effects after thermal incubation of dark chocoare below and above the meiting point of CB.

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<u>Key Words</u>: Chocolate, seeding, 308 crystal bowder, cocoa butter, polymorphism, fat bloom, tempering, triacylgiycerol.

Introduction

Chocolate consists of solid particles such as social, sugar, and milk solids which are dispersed in a continuous fat phase. In the case of dark chocolate, the milk solids are absent. The properties of chocolate are influenced by the size and distribution of the above solid particles, and by the crystallographic properties of the fat phase. In particular, fats influence heat-resistance, shap, gloss, quick and sharp melting in the mouth and bloom-resistance. Fat structures in chocolate have been investigated from various points of view (Huyghebaert and Hendrickx, 1971; Johnstone, 1972; Lovegren et al., 1976; Timms, 1980; Manning and Dimick, 1981; and Chaiseri and Dimick, 1989).

The major fat in chocolate is cocoa butter (CB). About eighty percent of C3 is composed of specific triacylglycerols (TAGs) of a Sat-O-Sat (saturated-oleicsaturated) type, such as POP (1,3-dipaimitoyl-2-oleoylgiycerol), POS (2-oleoyi-palmitoyl-stearoyl-giycerol), and SOS (1,3-distearoyl-2-deoyl-glycerol). CB, as a mixture of POP, POS and SOS, is polymorphic, revealing six forms (Forms I through VI), as identified by Wille and Lutton (1966). The polymorphic form of CB n the end products is Form V, since this form has the most desirable melting and solidification behavior compared to other polymorphs. Form V is not the most stable polymorph, form '/l is; therefore Form V transforms to Form VI either through a solid-state or a meltmediated transformation .Chapman, 1971). transformation to Form VI gives rise to undesirable onysical properties of the end products. Particularly, it causes fat bloom (Aronhime and Garti, 1988). Similarly, the less stable forms, such as Form III or Form IV crystailize more rapidly than form V (Wille and Lutton, 1966). The occurrence and transformation of less staple forms to Form V also result in undesirable effects, such as a non-temper type fat bloom. Therefore, control of colymorphic crystallization of CB on a manufacturing scale requires very careful thermal treatments.

In current practice, the chocolate industry uses

T. Koyano, I. Hachiya and K. Sato

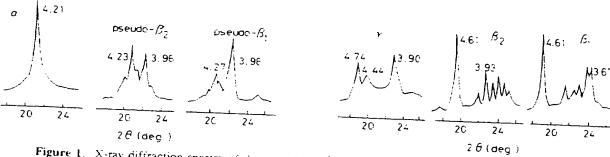


Figure 1. X-ray diffraction spectra of short spacings (A) for the polymorphs of POP (Sato et al., 1989).

two methods to control crystallization: tempering and seeding. In tempering, the completely melted (50-60°C) chocolate is first cooled to 27-28°C, then reheated to 30-32°C, where the chocolate is held so that all of the metastable forms of CB transform to Form V. Thereafter, chocolate is simply cooled to around 15°C for the final solidification. The seeding method is aimed at simplification of chocolate solidification with the aid of seed crystal powders.

In this review, we present: (1) a historical review of the seeding technique applied in the chocolate solidification process. (2) the physical properties of polymorphism of Sat-O-Sat TAGs, (3) the seeding effects of fat crystals on the solidification of dark chocolate, and (4) some of the improved properties of cnocolate produced by the new seeding technique, particularly fat bloom stability.

Historical Survey of the Seeding Techniques

The seeding method has so far been employed in small scale production, for example by local small candy makers or in small scale manufacturing trials. Small pieces of chocolate cut or shaved by knife have been employed as seed materials. Several fundamental studies have been devoted to analyze the seeding mechanism. Duck (1958) and Campbell and Keeney (1968) added chocolate powders to moiten chocolate and measured the viscosity changes in an attempt to estimate the amount of seed crystal formed during the tempering process. Hettich (1966) studied the relationship between the anti-bloom stability and the degree of tempering process.

None of these efforts, nowever, have been used in industrial chocolate manufacturing. This may be due to a lack of understanding of the complicated polymorphism of CB and its constituents, as well as the difficulties in producing, on a large scale, fine powders usable as seeding materials.

Polymorphic Crystallization of Four Sat-O-Sat TAGs and Cocoa Butter

In this section we discuss the polymorphism and melt crystallization of POP, SOS, AOA (1,3-diarachid-

oyi-2-oleoyi-giycerol., BOB (1,3-dibehenoyi-2-oleoyi-glycerol), and CB as well as SSS (tristearoyi-glycerol). These Sat-O-Sat TAGs exhibit essentially common polymorphic behavior which is closely related to seeding effects as described later.

Literature on the polymorphism of Sat-C-Sat TAGs contains serious contradictions (see Sato et al., 1989, and references therein). This is mainly attributed to the uncertain purity of the samples. Wang et al. (1987) identified five basic polymorphs: alpha (a). gamma (γ), and three forms of beta (pseudo- β), β_2 , and β_1) in POP, SOS, AOA and BOB with X-ray diffraction (XRD) and differential scanning calorimetry (DSC). Using the same methods, Sato et al. (1989confirmed the occurrence of the five basic polymorphs of POP and SOS in pure (99.9%) samples. In POP. however, the polymorphism was slightly modified. since there are two pseudo- $oldsymbol{eta}$ forms. Arishima and Sato (1989) grew crystals of β_2 and β_2 from acetonitrile solutions, clearly proving the occurrence of two eta forms. The differentiation of the two eta forms is directly related to Form V and VI of CB. Guth et al. (1989) confirmed the existence of the five polymorphs in SOS, examining the effects of addition of sorbitan monostearate on the divistallization of the SOS polymorphs.

The XRD patterns of six polymorphs of POP are shown in Fig. 1. The XRD patterns of forms a, γ, β_2 and β_1 of POP are nearly identical to those of SOS. AOA and BOB. The two pseudo- β forms differ from those of the other three TAGs. Melting points, XRD long spacing, and chair length structure of the four Sat-O-Sat TAGs are summarized in Table 1. From these observations we reach four conclusions:

(1) The chain length structure differs in different polymorphic forms. The least stable a forms have double chain length structure in all TAGs. The two pseudo-\$\beta\$ forms of POP are also double. The rest of the polymorphs are in the triple chain length structure. As depicted in Fig. 2, the saturated and oleoylacyi chains are packed in the same lamellar pattern in the double chain length, but they are separated in the triple chain length polymorphs.

(2) Melting points increase with increasing thermodynamic stability of the different polymorphs.

Table 1: Physical properties of polymorphs of Sat-O-Sat TAGs

Polymorph	n TAG	Melting point (°C)	Long spacing (nm)	Chain 'ength structure
a	POP	15.2	4.65	double
	SOS	23.5	4.83	double
	AOA	31.5	5.52	double
	BOB	41.5	5.61	double
Y	POP	27.0	6.54	triple
	SOS	35.4	7.05	triple
	AOA	45.5	3.04	triple
	BOB	49.5	8.41	triple
ρseudo-β′	POP (-B' ₂)	30.3	4.24	double
	POP (-B' ₁)	33.6	4.24	double
	SOS	36.5	7.00	triple
	AOA	46.5	7.60	triple
	BOB	50.5	8.03	triple
β_2	POP	35.1	6.10	triple
	SOS	41.0	6.50	triple
	AOA	46.6	7.07	triple
	3OB	53.0	7.36	triple
β ₁	POP	36.7	6.10	triple
	SOS	43.0	6.50	triple
	AOA	48.3	7.07	triple
	BOB	53.3	7.36	triple

POP has two pseudo-β' forms.

and with increasing chain length of the saturated part of the molecule.

(3) There are two β forms in each TAGs, which differ in melting point as well as in their XRD short spacing patterns (Fig. 1). Note that β_2 and β_1 were also found in a mixture system of POP/POS/SOS having a weight ratio of 18.2/47.8/34.0 (Sagi et al., 1989).

(4) The basic polymorphism in Sat-O-Sat TAGs is more complicated than that of SSS which has three double chain length polymorphs, α , β and β . Hagemann, 1988).

Compared with CB (Sato, 1987; Aronhime and Garti, 1988), Forms II, V and VI correspond to α , β_2 and β_1 of Sat-O-Sat TAGs, respectively. As for Forms III and IV, they seem to be equivalent to two pseudo- $\vec{\beta}$ forms of POP, as far as the XRD short spacing and the double chain length structure are concerned. Melt crystallization of POP and SOS

Before explaining the crystallization of dark chocolate, we describe the rate of melt crystallization of POP and SOS, since those data are closely related to the polymorphic crystallization of CB. Pure (> 99.9%) POP and SOS were examined with a polarizing

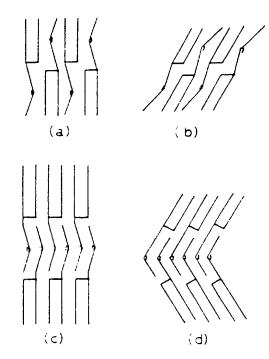


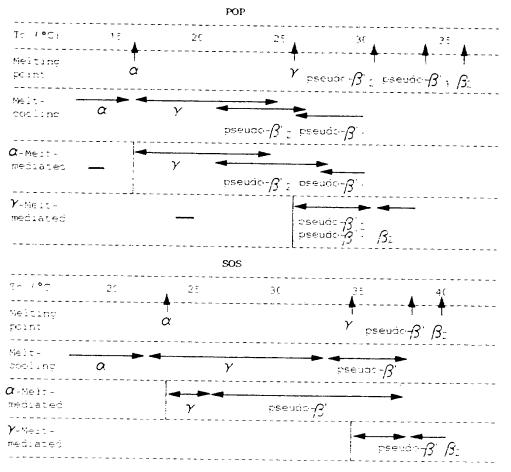
Figure 2. Postulated structure models of POP polymorphs: (a) α , (b) pseudo- β' , both are double chain length, (c) γ , and (d) β_2 and β_1 , which are triple chain length of POP (Sato et al., 1989). Unsaturated chains are indicated by dash (-) parallel to the chain.

obtical microscope equipped with a CdS photo sensor (Koyano et al., 1989). The sample was placed on a thermostated glass growth cell with the temperature controlled at a crystallization temperature $T_{\rm g}$. Obtically anisotropic crystals, shown in Fig. 3, were found. Fig. 4 shows a typical output of the photo sensor in the melt-cooling of POP measured at two $T_{\rm g}$ values. The polymorphic form of each crystallized sample was determined by XRD and DSC, in an attempt to clarify the polymorph-dependence of the crystallization rate. From Fig. 4, it is clear that the induction time r is shorter in the crystallization of p at $T_{\rm g} = 23.2^{\circ}{\rm C}$ than in the crystallization of pseudo-p' at $T_{\rm g} = 26.3^{\circ}{\rm C}$. The difference in the crystallization rate is also reflected in the time dependence of the photo sensor output.

Two methods of crystallization are applied, simple cooling and melt mediation. The latter involves the crystallization of the more stable forms, which were nduced after the melting of the less stable forms by rapidly raising the temperature. The tempering process may involve the melt-mediated transformation. The occurrence domains of the polymorphs of POP and SOS are summarized in Table. 2. Combining the accurate measurement of the crystallization rate of each polymorph. Koyano et al., 1989) and the results in Table 2, the following conclusions can be grawn:

T. Koyano, I. Hachiya and K. Sato

Table 2 Occurrence domains of polymorphs of POP and SOS from melt (melt-cooling and melt-mediated).



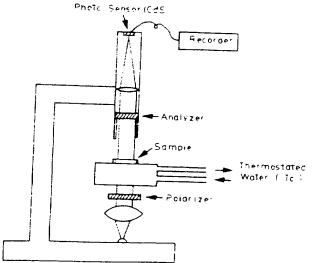


Figure 3 Optical system for induction time measurement of melt crystallization. (Koyano et al., 1989).

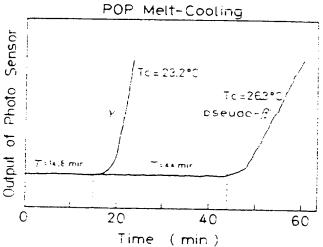


Figure 4 Output of photo sensor in case of simple cooling of POP at $T_c=23.2$ and 26.3 °C (Koyano et a 1989). The crystallization rates differ for the two polymorphs.

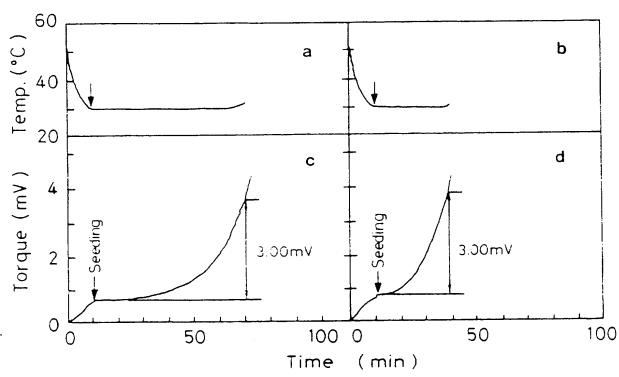


Figure 5. Changes of torque and temperature of dark chocolate seeded with SOS (β_1) at $T_1 = 30^{\circ}$ C. (a, c)(0.035) weight %, and (b, d)(0.5) weight % (Hachiya et al., 1989a).

- (1) The less stable forms crystallize more easily than the more stable forms by the two crystallization modes.
- (2) The rate is always higher in melt-mediated crystallization, than in simple cooling.
- (3) The rate of β_2 crystallization is extremely low in both POP and SOS.

From this, we assume that the first rapid cooling may cause the preferable crystallization of the less stable forms of CB in the tempering process of chocoate. These forms may transform to Form V through melt-mediated crystallization by the subsequent reneating process. This is proved by careful analysis as described below.

Cocoa Butter Crystallization in Tempering process

Some arguments have been presented to estimate the amount of CB crystals formed after the tempering procedure, assuming the optimal amount of seed crystals to be added in the seeding techniques. Hettich (1966) reported that 0.1% of CB is crystallized and that this quantity is most suitable for bloom resistance. On the other hand, Campbell and Keeney (1968) concluded that the amount is 0.5%. We used a rotational viscometer (Hachiya et al., 1988b) to measure the viscosity of the sample. Varying amounts of the CB seed crystals of Form VI were added, and the viscosity was recorded to make a calibration curve between the CB crystal concentration and the viscosi-

ty change. We concluded that the amount of the seed crystals crystallized in the tempering process was 0.2%.

Kinetics of seed Crystallization of Dark chocolate

We discuss here the crystallization behavior of dark chocolate seeded with five fat crystal powders: CB (Form VI), SOS (β_1) , BOB (β_2) , BOB (pseudo- δ) and SSS (β) . All of the measurement were made with a rotational viscometer (Hachiya et al., 1989b).

Figure 5 shows the torque value of dark chocolate which was crystallized at $T_c=30^{\circ}\text{C}$ by cooling the melt from 50°C. The seed powders of SOS (β_1) , with the concentration of 0.035 and 0.5%, are added at 30°C. It is clear that the rate of crystallization increases with increasing amount of the SOS (β_1) seed powders. In order to numerically express the rates of the seed induced crystallization in comparison to that of the non-seeded crystallization, we define the crystallization time (t_c) as the period when the torque increase (mV) due to crystallization reaches 3 mV.

Figure 6 shows the crystallization rate of dark chocolate seeded with five fat powders. The relative crystallization time (t_r) is defined as: $t_r = t_c$ (seeded) if t_c (non-seeded). The results show that the degree of acceleration goes in the following order: SOS $|\beta_1\rangle\approx$ CB (Form VI) > BOB $|\beta_2\rangle$ > BOB (pseudo- $|\beta|$) >> SSS $|\beta|$.

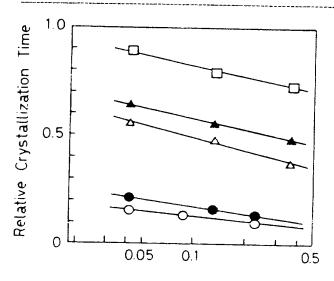
From this, it appears that two major factors.

T. Koyano, I. Hachiya and K. Sato

Table 3. Demoiding and fat bloom occurrence of seeded dark chocolate just after cooling at 15°C for 15 minutes.

Amount of crystal. Powder in percent*	Cocoa Butter (Form VI)		SOS (β ₁)		BOB (β ₂)		BOB (pseudo-β*)		SSS (β)	
	Demold- ing	Fat bloom	Demold- ing	Fat bloom	Demold- ing	Fat bloom	Demold- ing	Fat bloom	Demolo- ing	Fat bloom
0.001	good	sligh:	good	slight	bad	ves				
0.005	good	slight	good	slight	good	sligh:				
0.01	good	no	good	no	good	no				
.05	good	no	good	no	good	no	very bad	yes.	very bad	Noc
. 1	good	no	good	no	good	no		yes	very bac	ves
.5	good	no	good	no	good	no	bad	slight		
.0	good	no	good	no	good	no		31.2.11	very bad	1105
.5	good	no	good	no	good	по	good	slight	very bac	yes
.0	good	no	good	no	good	no	good	slight	very bad	yes

^{*}Amount with respect to fat content of dark chocolate.



Concentration of Seed Crystal (%)

Figure 6. Relationship between relative crystallization time of cocoa butter and concentration of seed materials at $T_c = 30^{\circ}C$: (\bullet) cocoa butter (Form VI); (\bigcirc) SOS (β_1); (\triangle) BOB (β_2); (\triangle) BOB (pseudo- β); (\square) SSS (β) (Hachiya et al., 1989a).

polymorphic structure and thermal stability, influence the crystallization acceleration in a combined manner (Hachiya et al., 1989a). As to the thermal stability it follows that the degree of acceleration increases with melting point. This factor becomes clear when one compares the two forms of BOB to each other, and SOS (β_1) with CB Form VI. However, this does not

apply to SSS (β) whose melting point is highest, nor to SOS (β_1) and CB (Form VI) whose melting points are lower than those of the two forms of BOB Hence the similarity in the polymorphic structure between the seed crystal and CB seems more determinative. No argument may be needed for SOS (β_1) and CB (Form VI). As to the two forms of BOB, their meiting points (Table 1) are far below that of SSS (73°C; Hagemann, 1988). But the molecular structures, particularly the triple chain length structure, of both forms of BOB are similar to those of CB. The lower acceleration effect of BOB compared to SOS and CB may be due to a difference in the chain length of the saturated portion of the molecules. The importance of the chain length structure is seen in the extremely low acceleration effect of SSS which is of the double chain which quite differs from the triple chain length of Form V of CB.

Consequently, it was concluded that seed crystallization of dark chocolate is highly dependent on the polymorphic properties of the seed materials. The most preferable seed material, in view of the crystallization rates are CB (Form VI), SOS (β_1) and BOB (β_2) .

Seeded Solidification Behavior of Dark Chocolate

Table 3 summarizes the degree of **demolding** and the occurrence of fat bloom of seed-solidified dark chocolate, examined just after the solidification. The dark chocolate **seeded at 30°C** is directly cooled at 15°C. The results are summarized as follows: CB (Form VI) and SOS (β_1) snow easy demolding and no fat bloom at seed concentrations above 0.01%. By contrast, undesirable properties were observed for BOB (pseudo- β) and SSS (β). From this observation,

Fat Bloom Stability of Dark Chocolate

Table 4A. Stability of fat bloom of dark enocolate seeded with cocoa butter (Form VI) and SOS (β_1) crystal powder.

Thermo-cycle condition		Amount of seed crystal powder (%)*							
i nei me	o-cycle condition	:).05	0.1	0.5	1.0	2.5	5.0		
	0 cycle	-		-	_				
	i cycle	-	-	-		_			
32°C (12 h)	2 cycles	-	-	-	-	- -			
† ↓	3 cycles	-	-	_	•	-+	· 		
20°C (12 ክ)	4 cycles		-	-	-		-		
	5 cycles	-	-	÷		÷ + ÷			
	6 cycles					++	+-		
38°C :12 h)	**********************		***************************************						
20°C (12 h)	i cycle			* * *	****	+-	 +		

Table 4B. Stability of fat bloom of dark chocolate seeded with BOB (\$\beta_2\$) crystal powder.

- Thermo-cycle condition		Amount of seed crystal powder (%)*						
		0.05	0.1	0.5	1.0	2.5	5.0	
	0 cycle		•					
	i cycle	-	-	-	-	_	_	
32°C (12 h)	2 cycles	+	-	-	*	_	_	
• •	3 cycles	+	-	-		-		
20°C (12 h)	4 cycles		÷	-		-		
	5 cycles		-	+	-	-	_	
	6 cycles		+	+		-	-	
38°C (12 h)				••••	******************			
20°C (12 h)	i bycie			++		-		

[&]quot;Amount with respect to fat content of dark chocolate (43%),

- : no fat bloom;

+ : fat bloom.

we conclude that CB (Form VI) and SOS (β_1) are most suitable; to a lower extent BOB (β_2) also showed good results at the level of 0.01%.

Anti-bloom Effects by Seeding

The effects of the fat crystal seeding on blooming of dark chocolate were examined using the seeds of CB (Form VI), SOS (β_1) and BOB (β_2) (Hachiya et al., 1989b). Two thermo-cycle tests were applied. In the 32/20 test, one cycle involves incupation of the sample at 20 and 32°C for 12 hours each. In the 38/20 test, the chocolate was kept at 38°C for 12 hours where the chocolate was completely melted, and 20°C for 12 hours.

The results are shown in Tables 4A and B. In all of the seed materials employed, bloom stability was confirmed at seed concentrations between 0.05% and 1%, being highly dependent on the seed materials. CB (Form VI) and SOS (β_1) show quite similar behavior, summarized as follows:

- (1) In the 32/20 test, fat bloom does not occur at seed concentrations of 0.05 through 1% below 4 cycles. However, fat bloom occurs at concentrations of 2.5 and 5%. The decrease is manifest at higher concentrations, in which the fat bloom occurs through one cycle.
- (2) In the case of the 38/20 cycle test, fat bloom occurs at all seed concentrations.

In contrast, seeding with BOB (β_2) gives rise to

significant stability against fat bloom through the 32/20 and 38/20 cycle tests, when the seed concentration is increased. In particular, the sample seeded at concentrations of 1, 2.5, and 5% does not produce fat bloom even through six cycles in the 32/20 test. In the case of the 38/20 test, the fat bloom is observed at low seed concentrations, but the seeding of 5% completely prevents fat bloom at one cycle (Fig. 7).

From these observations of the anti-bloom effects combined with the earlier results of crystallization kinetics, we conclude that the BOB (β_2) seeding shows two advantageous effects in the crystallization and transformation of the chocolate fats: the acceleration of the crystallization of Form V of CB, and the anti-bloom stability in temperature ranges below and above the melting point of CE

Application of BOB Seeding Techniques in Factory-Scale Chocolate Production

In this section, we review several aspects related to the application of the BOB seeding technique on the factory scale.

Solidification Process

No tempering machine is required in the seeding technique. Instead, the molten chocolate is cooled to 15°C in two steps. First, it is cooled to 33°C where seed is added. When the seed is added below 33°C, "over seeding" occurs, causing too enhanced crystallization. Then the seeded chocolate is cooled to 15°C. By controlling the amount of seed crystal, one may handle the chocolate solidification by simpler temperature control compared to the traditional tempering method.

Viscosity Change After Seeding

Viscosity of the chocolate during the solidification process is critically important for workability, which is greatly influenced by crystallization.

The traditional tempering method involves first cooling of the melt around 27°C, followed by neating around 30°C, and then the second cooling at 15°C. The crystallization during the first cooling is influenced by spontaneous nucleation of cocoa butter crystals. The induction time for nucleation scatters a lot and the occurrence of specific polymorphic modification is a result of competition of the rates of nucleation of different polymorphs. This uncertainty is particularly revealed in Form V of CB. Hence, its crystallization is attained by the transformation from the less stable Forms III and IV which crystallized during the first cooling. Accordingly, one has to be very careful with the cooling-neating-cooling steps in the tempering process.

In the seeding technique, however, the crystallization process is fairly controllable. This is demonstrated in the viscosity of seec-crystallized chocolate. Figure 8 compares the viscosity changes of dark chocolate made by the normal tempering and by the BOB.

 (β_2) seeding. Viscosity of the tempered chocolate begins to increase immediately after the completion of tempering. However, viscosity of the BOB (β_2) seeded chocolate gradually increase after an induction period of about 50 minutes. This is a clear advantage for the chocolate manufacturer because it permits easier plant operation.

Solubility of BOB (\$\beta_2\$) Crystals in Cocoa Butter

Solubilization of BOB (β_2) seed crystals in molten CB, being highly temperature dependent, diminishes the seeding effect. Figure 9 shows the solubility of BOB (β_2) and BOB (pseudo- β) crystals in molten CB (Mori, 1989). This shows that a portion of BOB (β_2) , when added at 5%, remains undissolved at 38°C. This result helps explain the anti-bloom effect in the 38/20 test (Table 4B).

Mouth Feel of Chocolate Seeded with BOB (B2)

There is no difference in the feel of the chocolate in the mouth when BOB (β_2) seed powders are used because, as shown in Fig. 10, their dimensions do not exceed 70 μm_s almost same as that for the other solid particles (cocoa mass, sugar, milk solids) in chocolate as shown by Hachiya et al. 1988a).

Production of BOB (B2) Seed Powders

BOB is presently produced from fatty acid esters containing behanic acid and high oleic oils by transesterification using an enzyme catalyst (Mori, 1989). The reactant is fractionated and concentrated. The enzyme esterified BOB is transformed to the polymorphic form β_2 by incubation. The fine powders of BOB (β_2) are produced with a cryo-mill (Fuji Powder: Atomizer Eli-75) which can pulverize at -60°C ~-100°C using liquid nitrogen (Hachiya et al., 1989c). The particle sizes are 20 ~ 70 μ m; no change in melting point was detected in powder samples.

The seeding method with BOB (β_2) fine powder (patented with US Patent 4,877,636 (1989); European Patent 87309981.6; and Japan Patent 63-240745; has now been in use in chocolate production plants of Japan.

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Fat Bloom Stability of Dark Chocolate

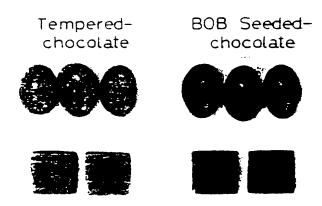
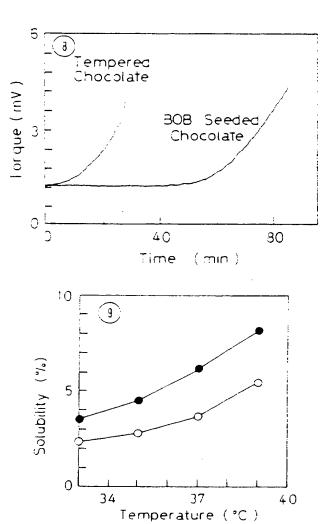


Figure 7. Photograph showing (a) bloomed chocolate normally tempered) at left; and b) hon-bloomed chocolate (BOB (β_2) seeded) at right; after thermotycle test of 38/20 for 3 cycles.



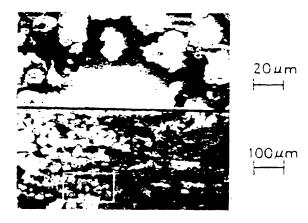


Figure 10. Cryo-scanning electron micrograph, taken at $-100^{\circ}\text{C} \sim -130^{\circ}\text{C}$ of BOB $-\beta_2$; powders pulverized at $-60^{\circ}\text{C} \sim -100^{\circ}\text{C}$.

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Figure 8. Viscosity changes in normally tempered chocolate and 8OB (β_2) seeded chocolate at 30°C. Figure 9. Solubility curve of 8OB drystal in cocolabutter \bullet BOB pseudo- β () (3) BOB β_2) (Mori, 1989).

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Discussion with Reviewers

J. Chevalley: BOB is not legally allowed in Europe and is not permitted in chocolate under current U.S. standards. Please comment on the legal aspects of BOB. Authors: Only Japan allows to add BOB seeds, all of the other countries do not. Meiji and Fuji Oil are now requesting the approval of the Food and Drug Administration in the United States and similar agencies in other countries. Fat bloom is facsinatingly improved with BOB seed, as Meiji has observed in the market.